

Contents

1	Porphyrins	1
1.1	Triplet State Properties of Free-Base Porphin	1
1.1.1	Method of Calculations	3
1.1.2	Singlet–Singlet Absorption	5
1.1.3	Prediction of Phosphorescence Radiative Lifetimes	6
1.1.4	Fine and Hyperfine Structure of the 1^3B_{2u} State	8
1.1.5	Solvent Effects on the Hyperfine Coupling	11
1.1.6	Discussion	11
1.1.7	Conclusions	12
1.2	Isomerisation of Free-Base Porphin	14
1.2.1	Method of Calculations	18
1.2.2	Results and Discussion	19
1.2.3	Conclusions	23
	References	23
2	Exohedral Metallofullerenes	27
2.1	Monoatomic Doping	27
2.1.1	Method of Calculations	28
2.1.2	Results	30
2.1.3	Discussion	35
2.1.4	Conclusions	40
2.2	Multiple Doping	40
2.2.1	Overview	40
2.2.2	Computational Details	41
2.2.3	Results and Discussion	41
2.2.4	Conclusions	44
	References	45

3	Nonlinear Optical Properties of Fullerene Derivatives	49
3.1	Computational Methods	51
3.1.1	Basic definitions of L & NLO properties	51
3.1.2	Electronic Contributions	52
3.1.3	Vibrational Contributions	53
3.1.4	Two-Photon Absorption	55
3.2	Fullerene-Benzothiadiazole and -Carbazole Derivatives	55
3.2.1	Structure of Investigated Molecules	56
3.2.2	Electronic Contributions to (Hyper)Polarizabilities	56
3.2.3	One- and Two-Photon Absorption Spectra	63
3.2.4	Vibrational Contributions to Electric Polarizabilities	72
3.3	Conclusions	74
3.4	Triphenylamine-Functionalized Fullerenes	75
3.4.1	Synthesis	77
3.4.2	Theoretical Methods	79
3.4.3	Nonlinear Optical Measurements	79
3.4.4	One-Photon Absorption Spectra	80
3.4.5	Nonlinear Optical Properties	83
3.4.6	Conclusions	88
	References	90
	Supplementary material	96
4	Endohedral Metallofullerenes	99
4.1	Methods of Investigation	100
4.2	Results and Discussion	103
4.2.1	Geometry Optimization	103
4.2.2	Electronic Properties	104
4.2.3	NR Contribution to Vibrational NLO Properties	107
4.3	Conclusions	109
	References	110
5	Fullerene-Porphyrin Dyads	113
5.1	Polyalkyne Chained Dyads	113
5.1.1	Computational Details	114
5.1.2	Results and Discussion	115
5.1.3	Conclusions	119
5.2	Polyacetylene Chained Dyads	120
5.2.1	Results	120
5.2.2	Conclusions	121
	References	122
6	Linear Scaling Methodology	123
6.1	Outline of Elongation Method	125
6.2	Elongation Method Deficiency	129

6.3	Orbital Basis Concept	130
6.4	Eigenvalue Problem	132
6.5	Applications	137
6.5.1	SW-BN/CNT	137
6.5.2	Polyacene	139
6.5.3	β -carotene	140
6.5.4	Lycopene	141
6.5.5	Fullerene–Polyacetylene–H ₂ TPP	145
6.5.6	Fullerene–Oligo(2,5-thienylene-ethynylene)–H ₂ TPP	145
6.6	Conclusions	148
	References	148

Quantum-chemical studies on Porphyrins, Fullerenes
and Carbon Nanostructures

Loboda, O.

2013, XVIII, 154 p., Hardcover

ISBN: 978-3-642-31844-3